

Biomaterial Course

Biomaterials Surfaces

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Final Year Bachelor of Chemical Engineering

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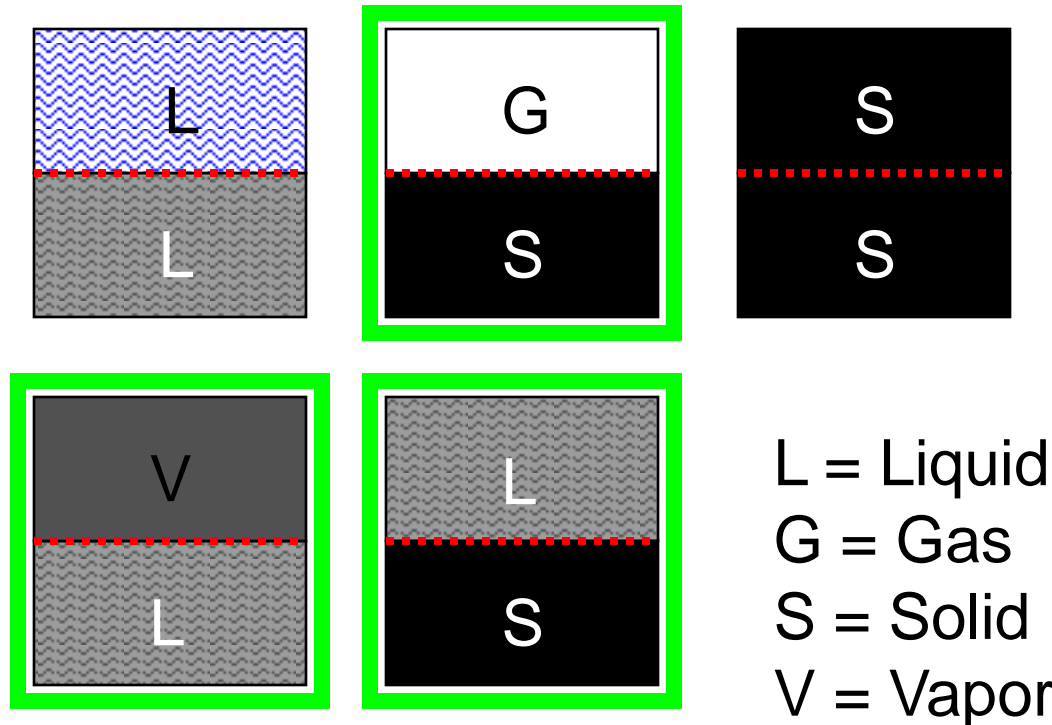
Reading

- 1) B. Ratner, A. Hoffman, F. Schoen, and J. Lemons:
Biomaterials Science,
2nd/3rd Edition edition (San Diego: Elsevier Academic Press.
2004).

- 2) Butt, H-J.; Graf, K.; Kappl *Physics and Chemistry of
Interfaces, 2nd Edition*
(Wilet-VCH: Weinheim 2006).

What constitutes a surface?

An **interface** is the boundary region between two adjacent bulk phases



We recognize (S/G), (S/L), and (L/V) as surfaces

Physical Description of Biomaterial Surfaces

Biomaterial surfaces exhibit remarkable heterogeneity in physical structure:

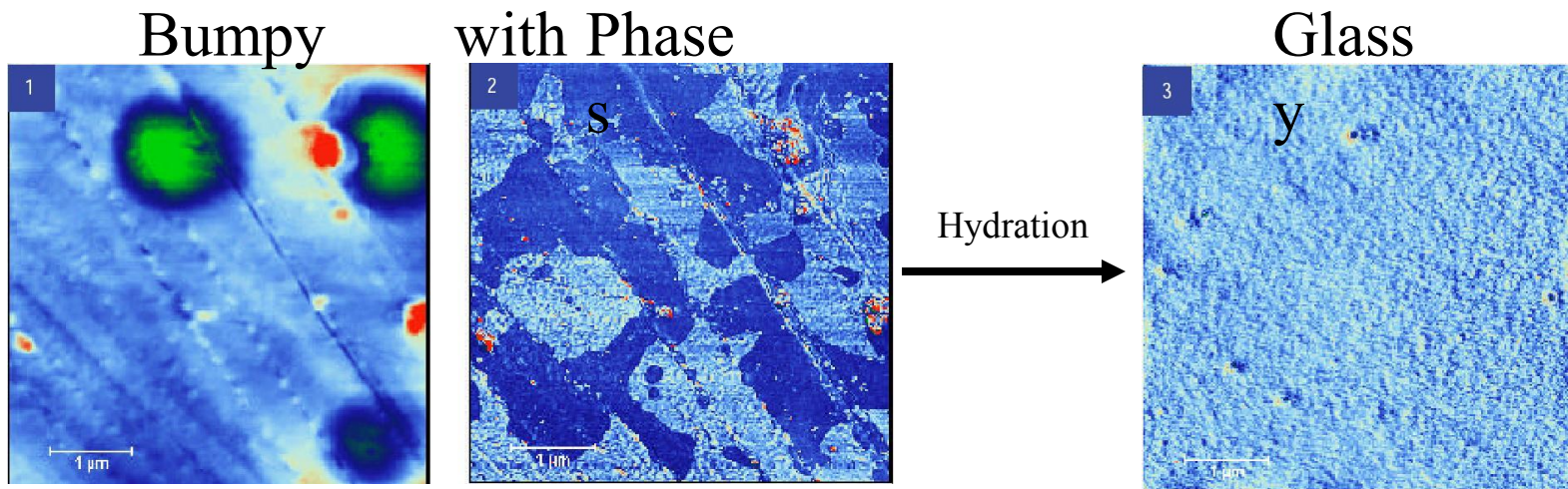
Material dependant: Metals vs. Polymers vs. Ceramics vs. Gels

Chemistry: Polar vs. Apolar, Charge, Reactivity, Patterned

Morphology: Smooth, Rough, Stepped, Patterned, Diffuse

Order: Crystalline, Amorphous, Semi-Crystalline, Phases

Environment: Hydration, Solvent Quality



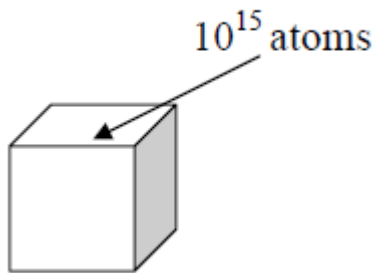
Bulk Vs Surface

The success or failure of many biomaterials depends on the

- Physical and chemical characteristics of their surface.
- It is the surface properties that dictate interactions between a material and its environment, and thus whether a permanently implanted material will be tolerated or rejected.
- In cases where the implanted material is required to degrade at a controlled rate (e.g., when the implant is a temporary support, such as a dissolving suture or a scaffolding for cells that regenerate tissue),
- Then the bulk material must be capable of sustaining those properties continuously as it becomes the new surface.

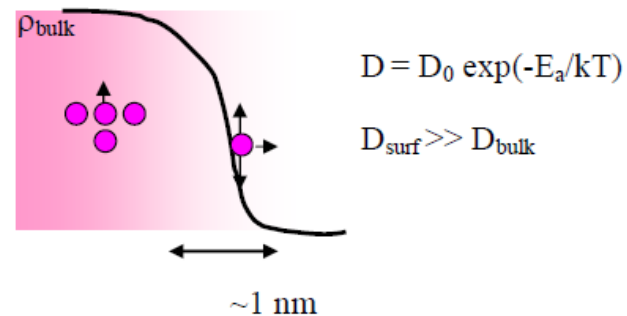
Microstructure and Properties

The bulk properties of a material depend not only on what types of atoms and molecules it contains (composition), but also on how those atoms and molecules are arranged (microstructure)



**Inherently
Small # of
Atoms**

1 cm³ material ~
10²³ atoms



Enhanced Mobility: fewer bonds ,
gradient in density

The microstructure of a material is a specification of the structural features at length scales that cannot be discerned with the naked eye.

Bulk Properties

Some bulk properties, such as the stiffness of a metal, depend principally on the type (composition) of metal being characterized, and not on the microstructure. Such properties are referred to as intrinsic properties, and they include density and heat capacity.

Other bulk properties, such as the yield strength of a metal, depend on attributes such as the average grain (crystal) size, as well as the number and distribution of defects in the crystal structure.

Yield strength is an example of an extrinsic property

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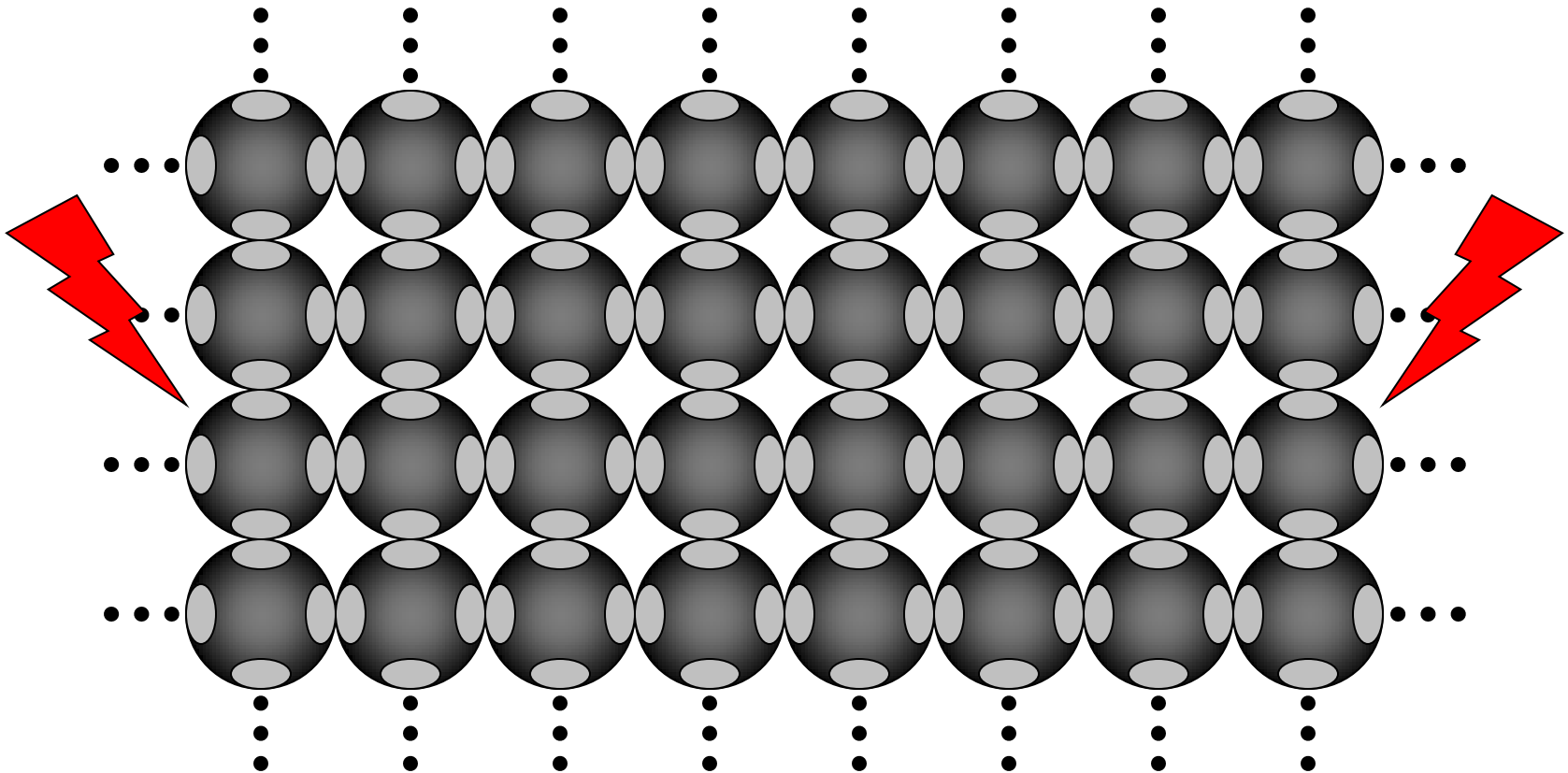
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Surface Energetics

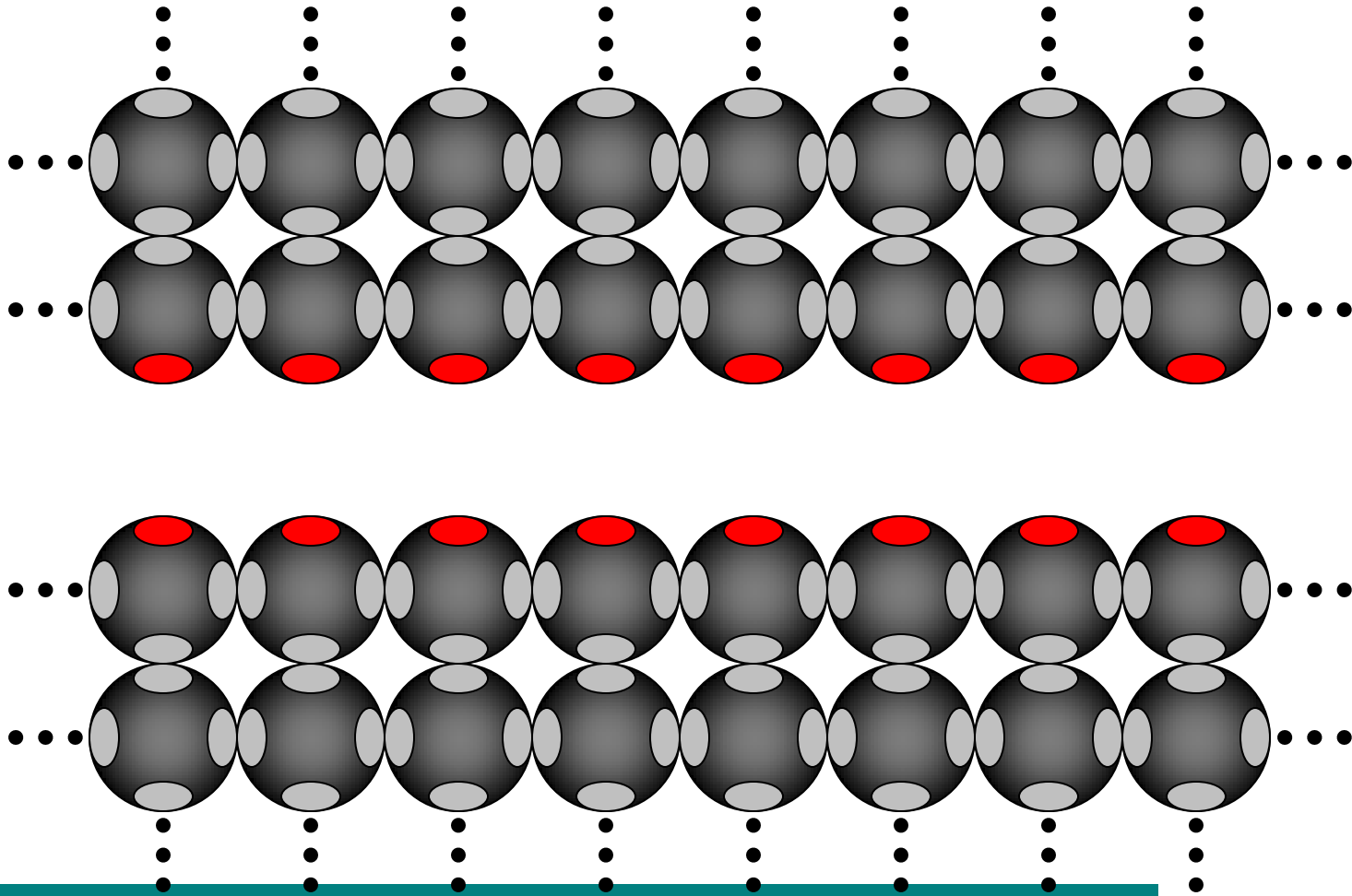
Molecules in the bulk of a material (e.g. crystal lattice) have a low relative energy state due to nearest neighbor interactions (e.g. bonding).

Performing sufficient work on the system to create an interface can disrupt this harmony...



(Excess) Surface Free Energy

Molecules at a surface are in a state of higher free energy than those in the bulk. This is in large part due to the lack of nearest neighbor interactions at a surface.

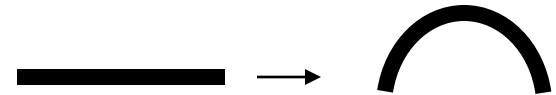


Important Point

Systems move toward lowering their free energy

Surfaces do so by:

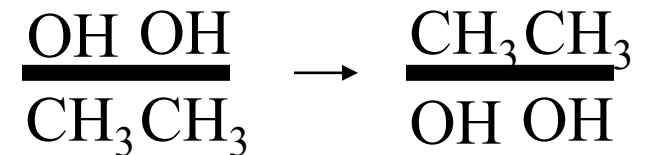
Geometric changes (if possible)



Bonding (strong and weak interactions)



Dynamic rearrangement



Surface Energy and Tension in Liquids

In order to develop some concepts related to surfaces we will first look at the surface properties of liquids.

The work (w) required to create a new surface is proportional to the # molecules at the surface, hence the area (A):

$$\delta w = \gamma \cdot \delta A$$

Where γ is the proportionality constant defined as the specific surface free energy. It has units of (force/unit length, mN/m) or (energy/unit area, mJ/m²).

γ acts as a restoring force to resist any increase in area, for liquids it is numerically equal to the surface tension.

Surface tension acts to decrease the free energy of the system, hence some observed effects:

- liquid droplets form spheres
- Meniscus effects in capillaries

Surface Tension of Solids

Bottomline:

The surface tension of solids is experimentally inaccessible.

Why?

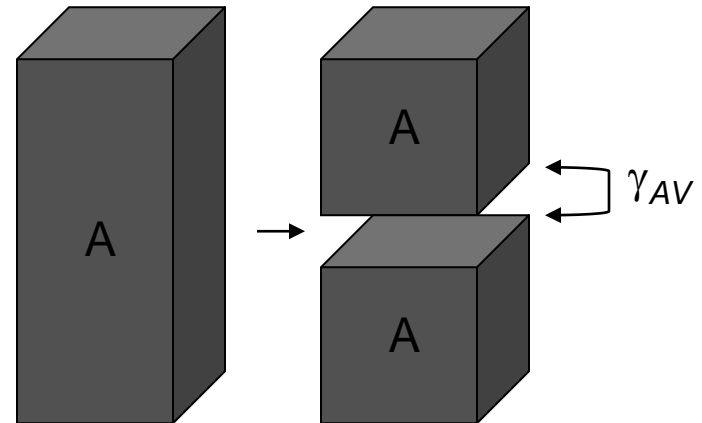
Creation of new area in a solid is not reversible – you end up stretching or cleaving the sample. Interfacial stress during elastic enlargement can be measured and related to interfacial tension only if the relationship of interfacial tension as a function of strain is independently known.

Work of Cohesion and Adhesion

Cohesion is the property of like molecules (of the same substance) to stick to each other due to mutual attraction. Adhesion is the property of different molecules or surfaces to cling to each other.

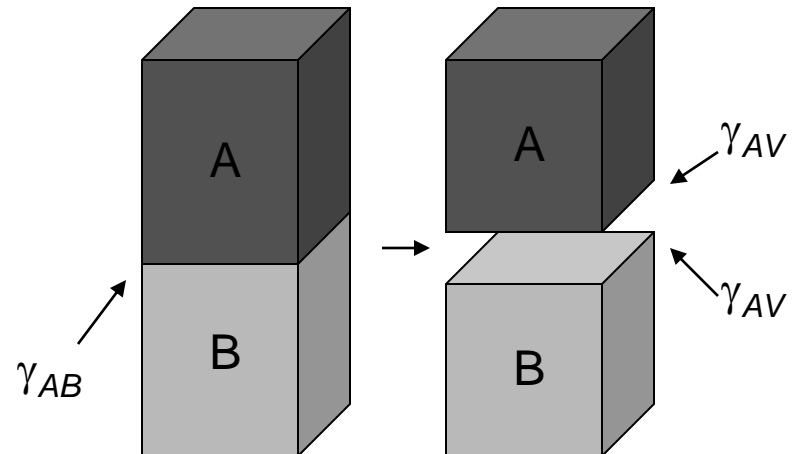
For a single liquid (cohesion):

$$W_{AA} = 2\gamma_{AV}$$



For two different liquids (adhesion):

$$W_{AB} = \gamma_{AV} + \gamma_{BV} - \gamma_{AB}$$



(V = vapor)

Surface Phenomenon

Surface phenomena are driven primarily by an associated reduction in surface free energy

Important examples in biomaterials:


- adsorption of a species from environment
- surface segregation of a species from bulk
- surface reconstructions
- surface reactions

Adsorption phenomena

- **Tenet 1:** Higher energy surfaces are quickly coated/contaminated by lower energy species

Examples:

- 1) Water on glasses, metals or oxides
- 2) Hydrocarbons on inorganic surfaces
- 3) Surfactants at air/water interface



Measured γ of
metals and oxides
 $\approx 37 \text{ dyn/cm}$

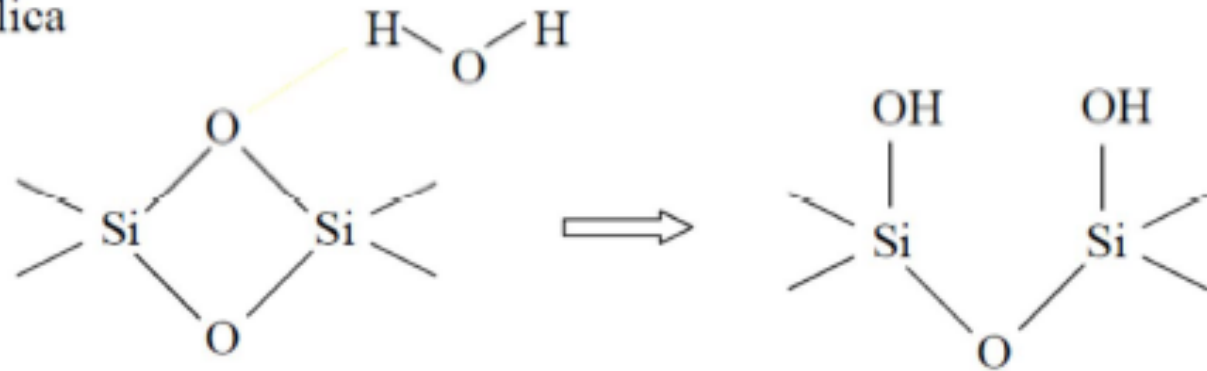
Classes of adsorption

1) **Chemisorption** – strong modifications to electronic structure/electron density of adsorbant molecule (> 0.5 eV/surface site)

- Process driven by a chemical reaction occurring at an exposed surface
- A new chemical species is generated at the adsorbant surface

Example: H_2O on silica

$$E_{\text{ads}} = 1.7 \text{ eV}$$



Classes of adsorption

2) **Physisorption** – adsorbate weakly adherent via secondary interactions (i.e. van der Waals') (< 0.25 eV/surface site)

- Physisorption is a general phenomenon and occurs in any solid/fluid or solid/gas system

Example: PMMA on silica

$$E_{\text{ads}} = 0.1 \text{ eV/mer}$$



N' mers adsorbed $\times 0.1 \text{ eV/mer} \approx$ total adsorption energy

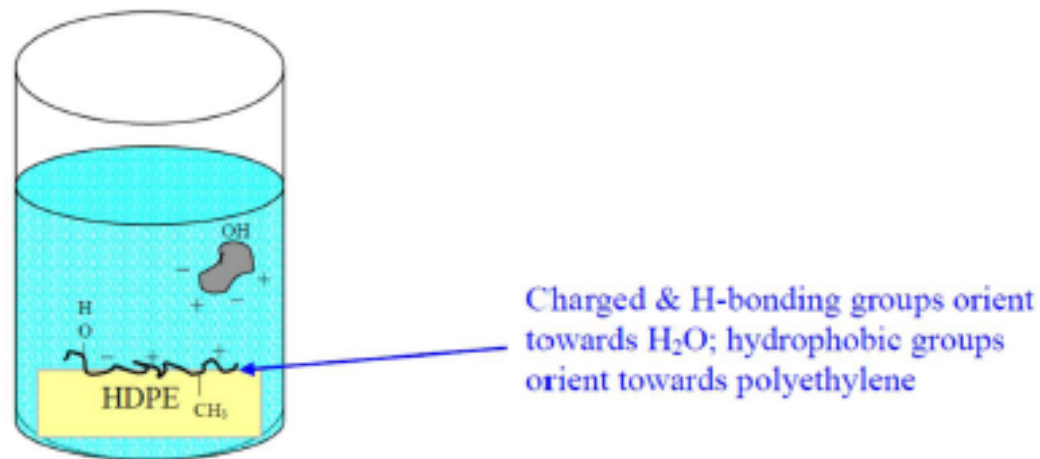
$$N' < N \text{ (segments/chain)}$$

Adsorption phenomena

- **Tenet 2:** The “high energy surface” of tenet 1 is relative to its surrounding medium

In H_2O based environments, a hydrophilic materials has a lower interfacial energy than a hydrophobic material

Example: Adsorption/denaturing of proteins on hydrophobic surfaces in water-based environments



Such adsorption phenomena are examples of “thermodynamic adhesion”
Thermodynamic adhesion is driven by interfacial forces associated with reversible processes.

ΔG_s can be estimated from the Miedema eqn:

$$\Delta G_s = -0.24 \left[\Delta H_{mix} + (\gamma_{A,SV} - \gamma_{B,SV}) 6N_{Av}^{1/3} V_{m,B}^{2/3} \right]$$

↑
prefactor is fraction of
atom contacting vacuum

$\Delta G_s > 0$ no surface
enrichment of B

$\Delta G_s < 0$ surface
enrichment of B

Metal surface tensions can be estimated from:

$$\gamma_{B,SV} = \frac{\Delta H_{sub}}{6N_{Av}^{1/3} V_{m,B}^{2/3}}$$

↙
molar volume

The Miedema model is ~90% accurate in
predicting segregation in AB alloys.

Source: *Interfaces in Materials*, J.M. Howe, John Wiley
& Sons: NY (1997) pp. 156-168.

Surface Segregation

Segregation in materials refers to the enrichment of a material constituent at a free surface or an internal interface of a material. In a polycrystalline solid, a segregation site can be a dislocation, grain boundary, stacking fault, or an interface with a precipitate or secondary phase within the solid. There are two recognized types of segregation: equilibrium segregation and non-equilibrium segregation.

- Surface segregation: an interfacial adsorption phenomenon involving a bulk component of a multicomponent material

Example 1: Surface segregation of a dilute solute (B) in a binary AB alloy

Surface fraction of B ($X_{B,S}$) can be described using the Langmuir-McLean relation:

$$\frac{X_{B,S}}{1 - X_{B,S}} = \frac{X_B}{1 - X_B} \exp \left[\frac{-\Delta G_S}{RT} \right]$$

where ΔG_S = free energy of segregation per mole of solute.

Surface enrichment is given by:

$$\frac{X_{B,S}}{X_B} \approx \exp\left[\frac{-\Delta G_S}{RT}\right]$$

$$\ln X = 2.3 \log_{10} X$$
$$R = 8.314 \text{ J/mol}\cdot\text{K}$$

The predicted behavior is more transparent by expanding the exponential...

$$\frac{X_{B,S}}{X_B} \approx 1 - \frac{\Delta G_S}{RT} + \dots$$

The Langmuir-McLean relation indicates:

- Surface enrichment occurs when ΔG_S is negative
- Surface coverage increases with bulk solute content
- Surface enrichment decreases with increasing T

In polymers, **ENTROPY** can play a significant role in surface segregation.

Polymer “random coil” conformations are restricted by the presence of a surface

⇒ **Less chain configurations!**



Chain ends surface segregate to decrease entropic penalty



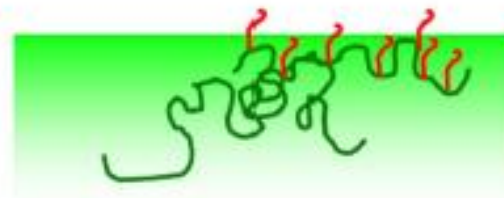
Short chains surface segregate when mixed with long chains



Surface segregation importance to biomaterials applications:

- **Toxicity**
- **Corrosion resistance**
- **Modified protein/cell adhesivity**

Surface modification with a comb polymer additive



But...also *a strategy* for surface modification!

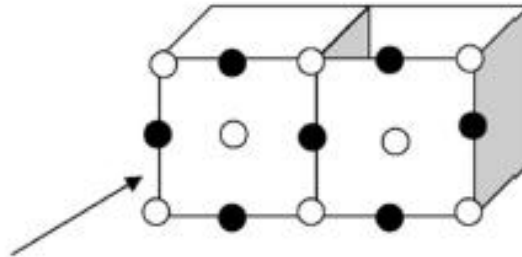
Surface Reconstruction

Atomic or molecular rearrangement at surface to reduce surface/interfacial tension.

Example 1: Faceting in MgO

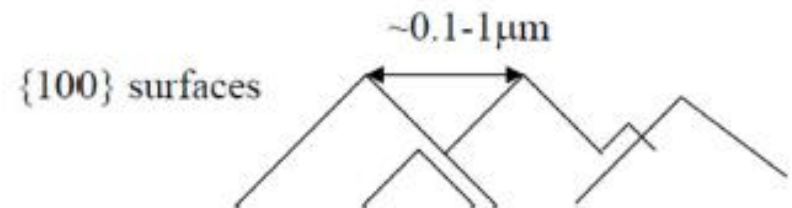
Rocksalt structure

○ = O^{2-} (fcc lattice pts)
● = Mg^{2+} (octahedral interstices)



(100) is preferred plane of cleavage (charge neutral!)

Miscut surfaces will facet



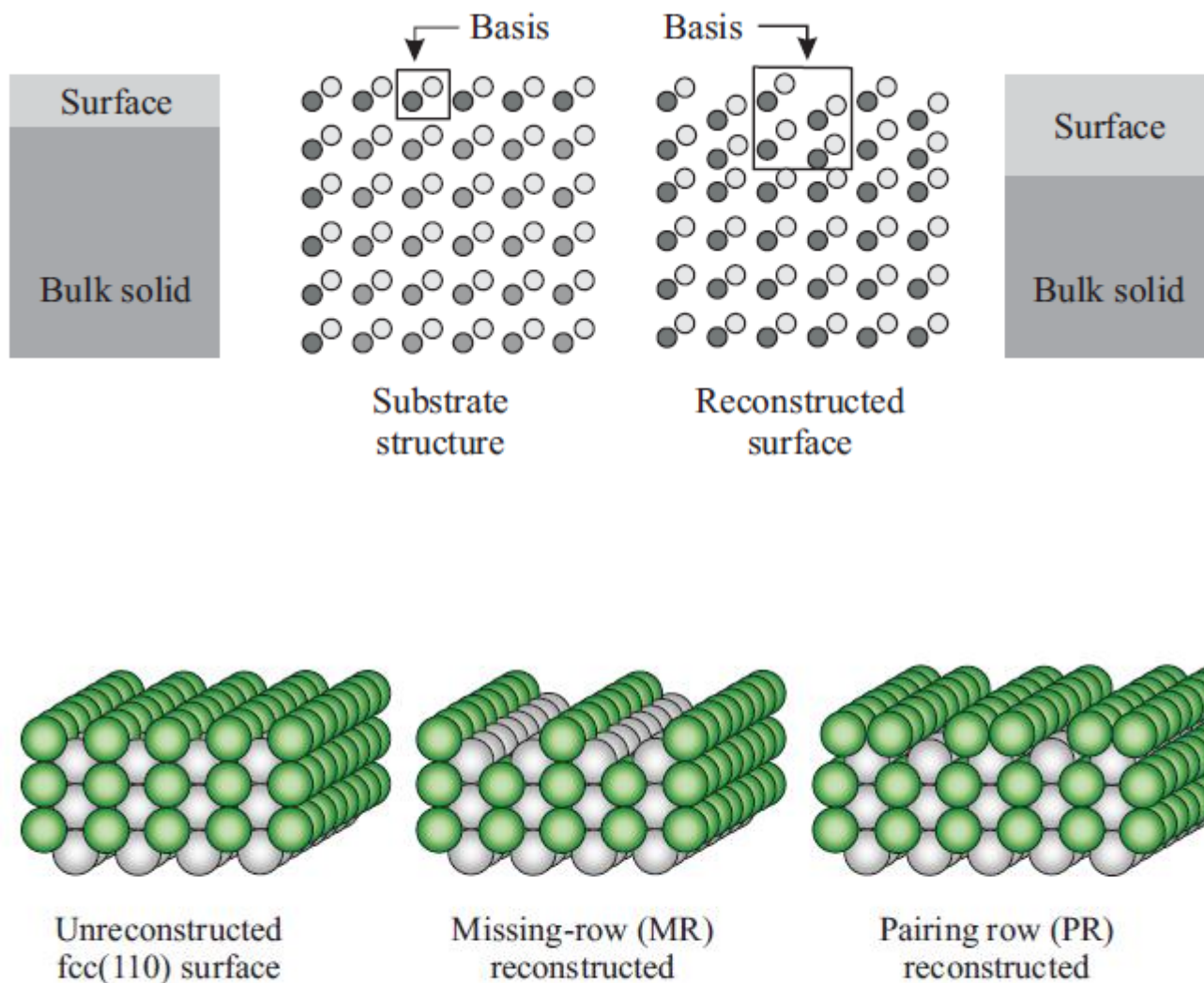


Figure 8.4: Typical reconstructions of face centered cubic (110) surfaces.

Surface Reconstruction

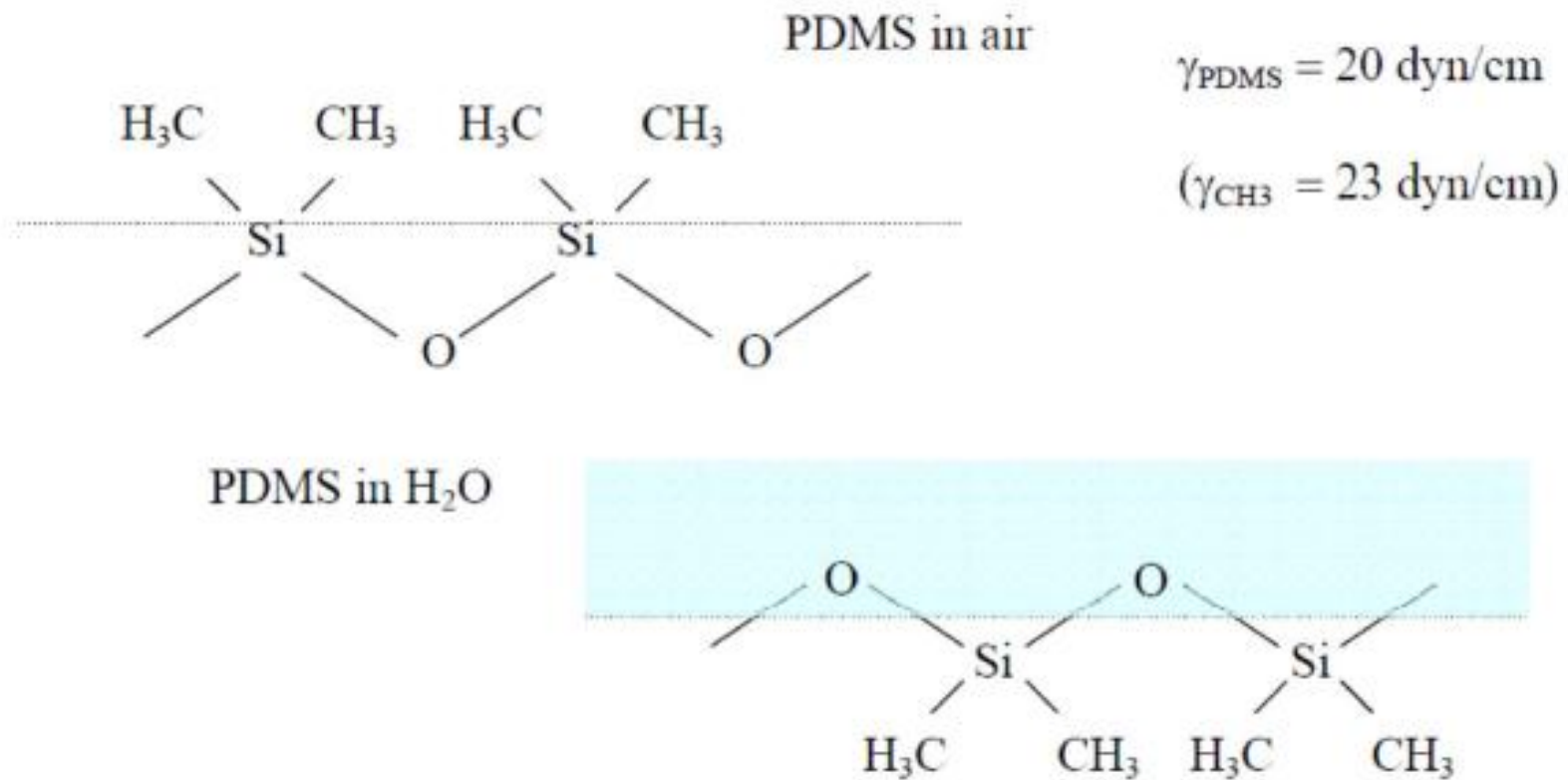
Oxides surfaces reconstruct to achieve:

- 1) no net dipole moment
- 2) minimal loss of nearest neighbor ligand coordination

Low Energy Oxide Surfaces

| Structure | low γ plane | Examples |
|---|--------------------|--|
| M ₂ O ₃ corundum | 10 $\bar{1}$ 2 | Ti ₂ O ₃ , V ₂ O ₃ , Fe ₂ O ₃ , Al ₂ O ₃ , Cr ₂ O ₃ |
| MO ₂ rutile | 110 | TiO ₂ , SnO ₂ |
| MO rocksalt | 100 | MgO, CaO, CoO |

Example 2. Reorientation of polymer chains in water vs. air



Chain reorientation can be observed with dynamic contact angle studies:

Thank You